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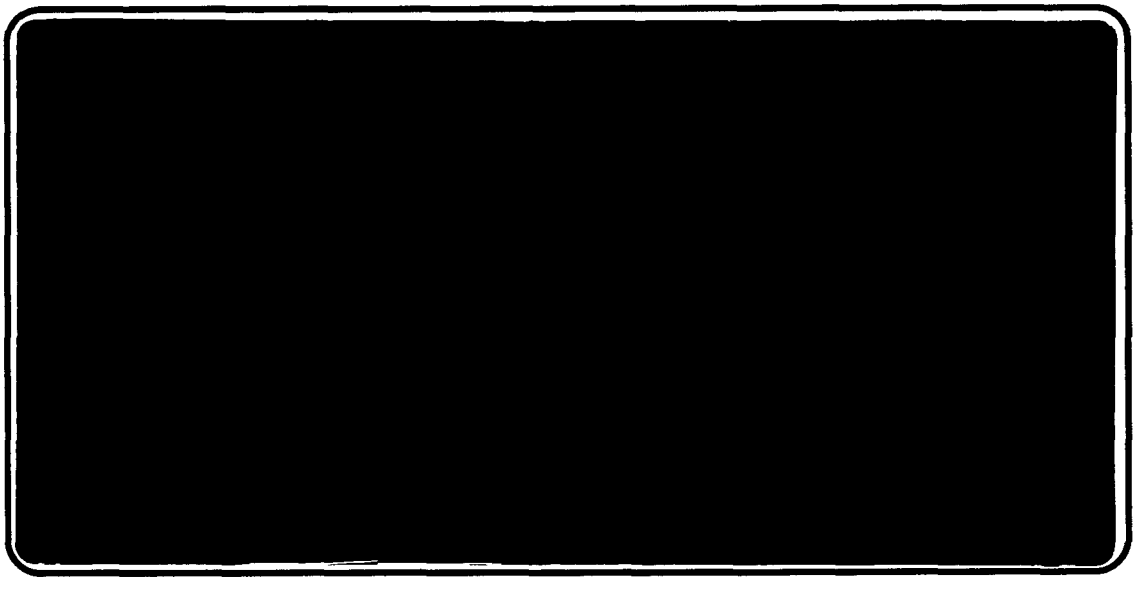

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GENERAL STRUCTURE-VAPOR PRESSURE RELATIONSHIPS FOR ORGANICS

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General Structure -Vapor Pressure Relationships for Organics

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General Structure-Vapor Pressure Relationships for Organics

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Abstract

Relationships between vapor pressure and (a) solvatochromic parameters and (b) UNIFAC derived variables are described. For the UNIFAC based equations, solute self-association in the condensed phase is modeled by calculating the interaction of the solute in a reference matrix of methyl groups. An expression for vapor pressure (r=0.99) ranging over 12 orders of magnitude and covering a wide variety of structures is developed. Boiling points are estimated through an analogous algorithm. Experimental data obtained by the gas saturation method are reported for 10 compounds.

Vapor pressure is important in disciplines ranging from analytical chemistry to inhalation toxicology, and there is a frequent need to estimate vapor pressure from structural or other parameters. Good structure-vapor pressure correlations exist in the engineering literature (1-6), but only for sharply defined families of compounds, and a general reliable algorithm is unavailable.

The vapor pressure of a compound depends principally on its size and on the degree of self-association in the condensed phase. Estimating the associative contribution is difficult, since polarizability, hydrogen bonding and other factors need to be considered. In preliminary work (7) we found that vapor pressure, VP (mm, at 25^{o}C) can be correlated with the Kamlet-Taft solvatochromic parameters (8) through eq 1

$$\log VP = 7.82 - 7.29\ (V_I/100) - 6.41\ \pi^* + 3.25\ \pi^{*2} \qquad (1)$$
$$- 0.01\ (mp-25) \qquad n=53;\ r=0.98$$

where V_I is molecular volume, π^* is a measure of solute dipolarity/polarizability and mp is melting point in ^oC. Equation 1 implicitly assumes that the entropy of vaporization is constant, i.e. Trouton's rule is obeyed. The melting point (mp) term is an entropy of fusion correction. It allows solids to be considered as hypothetical liquids and enables both liquids and solids to be covered by the same equation (9). Liquids are assigned a mp of 25 to remove the last term in eq 1.

Equation 1 was developed from structurally different compounds ranging over 12 orders of magnitude in vapor pressure, and the relationship is illustrated in Figure 1. The quadratic dependence on π^* was unexpected, and could not be interpreted in fundamental terms. Also, while solvatochromic parameters are remarkably versatile in that they correlate a wide range of properties, they are available for only a limited number of compounds. Nonetheless, Figure 1 demonstrates the feasibility of developing a general vapor pressure correlation from structural parameters.

Molecular size and self-association can also be obtained through the UNIFAC approach (10) which offers access to a wider range of structures. UNIFAC is a group contribution technique. Components in a given mixture are fragmented into groups, the properties of the groups are calculated, and the components are

then reconstructed from the groups. Since a variety of structures can be assembled from the same groups, mixtures can be handled almost as easily as pure compounds.

Group areas and volumes are required in UNIFAC, as are parameters for the interaction of every group with every other group in the mixture. The activity coefficient γ of a component is expressed as eq 2

$$\gamma = \gamma_C \gamma_R \qquad (2)$$

where γ_C, (the combinatorial), represents size/shape differences between the component and its matrix, and γ_R (the residual) reflects interactive effects.

The activity coefficients cannot be used directly since γ=1 for pure compounds. However, consider a situation where solute infinite dilution activity coefficients are calculated in an inert matrix. If the solute-matrix interaction parallels the solute-solute interaction, then a means for estimating solute self-association will be at hand. The approximation will be tenuous for solutes that participate in hydrogen-bonding, dipolar and other specific interactions. Nevertheless, we will show that these effects can be factored out to yield an algorithm that is both general and reasonably accurate.

Experimental

Vapor pressures were measured by the gas saturation method (11). Here, gas flows through a tube packed with the test compound. The saturated gas is then passed through a two-stage trap

where the compound is removed. The amount of material transported by a known volume of gas is related to the vapor pressure. Trapping is assumed to be complete if all the material is removed from the gas in the first stage.

Test compounds were provided by the National Institute of Standards and Technology. For the saturation step, samples were loaded into 50 mm glass tubes (5 mm id.) held between glass wool plugs. Liquids were first coated on glass beads by shaking an ether or hexane solution of the sample with the beads and then removing the solvent. The tubes were connected by ground glass ball-and-socket joints to two traps in series containing 4 cm. and 2 cm. of sorbent (either Tenax-GC or Lichrosorb RP-2) respectively. Three of these assemblies were held in an insulated wooden box maintained in a constant temperature room (± 0.5^{o}C).

Prior to the start of the experiment, the apparatus was temperature-equilibrated for several hours. Measurements were made concurrently at 3 flow rates spread over a threefold range. Flow was regulated by needle valves and averaged over the duration of the experiment. At the end of the saturation period which varied between 1-150 hours, the trapping material was removed, and the analyte was desorbed from each trap and determined by GC, GC-MS or HPLC. Corrections were made for the desorption efficiency which varied between 70-100%.

The results are reported in Table I, and the uncertainties are from measurements made over the 3 flow rates. Substantial breakthrough to the second trap occurred for DDT and dibutyl

phthalate, and these results could be underestimated. The value for 2,4-dinitrophenol is probably also an underestimate. The material contained a trace of an isomeric impurity which was much more volatile than the component of interest, and concentrated in the trap.

UNIFAC calculations were made through a program (obtained from BRI) which accepts structures in SMILES notation (12). The program incorporates the VLE parameters of Tiegs et al. (13) and references cited therein. Vapor pressures were obtained from the CHEMFATE database at Syracuse Research Corporation (14). Only experimental values that were either measured at 25° or could be interpolated to 25°C were selected.

Results and Discussion

The reference matrix is intended to be a general backdrop for a wide range of compounds, and it should be symmetrical and inert (i.e. without any functionality) to minimize bias. The methyl group fulfills these criteria, and infinite dilution combinatorials and residuals were calculated for the compounds in Table II in a hypothetical matrix of methyl groups. The results led to

$$\log VP = 7.02 - (2.27\ V_U + 4.26 \log \gamma_C) - 0.590 \log \gamma_R - 0.01\ (mp-25) \qquad (n=120;\ r=0.95) \qquad (3)$$

where V_U is the UNIFAC volume term which is related to molecular volume. The correlation is illustrated in Figure 2.

The bracketed term in eq 3 makes the principal contribution

to VP. V_U is related to log γ_C (r=0.97), and the purpose of including both quantities is only to improve fit. Without the log γ_C term, r drops to 0.90. We emphasize that eq 3 is empirical. The bracketed term and the residual are intended to reflect solute size and self-association, respectively, and further interpretation is not warranted.

Some of the major outliers from eq 3 are listed in Table III. Values for the carboxylic acids are overestimated, probably because hydrogen bonding is not accounted for. Estimates for the two siloxanes are unacceptable, and these compounds were excluded from the data used to generate eq 3. Also, eq 3 takes no account of gas phase association (which occurs, for example, for acetic acid), and assumes that Trouton's rule is obeyed.

Since boiling point (BP) is the temperature at which vapor pressure equals atmospheric pressure, a relationship analogous to eq 3 is expected for BP. We obtained

$$\log BP = -166 + 117\ V_U + 235 \log \gamma_C + 22.3 \log \gamma_R \quad (n=108;\ r=0.95) \qquad (4)$$

for the compounds in Table II for which boiling points were available; the equation is illustrated in Figure 3. As expected, many of the outliers from eq 4 were the same as those in eq 3, as shown in Table III. However, the deviations are systematic; values that are too high in the vapor pressure correlation are underestimated in the boiling point correlation. This provides a convenient means of correcting eq 3 through the deviations ob-

served in eq 4.

Equation 3 becomes

$$\log VP = 6.96 - 2.25\ V_U - 4.24 \log \gamma_C - 0.549 \log \gamma_R - 0.0193(BP - BP_{calc}) - 0.01\ (mp-25) \quad (n=108;\ r=0.99) \qquad (5)$$

where BP_{calc} is the boiling point calculated from eq 4; the relationship is illustrated in Figure 4. Equation 5 successfully handles the compounds in Table III which were outliers from equation 3. Even the large deviations for the silicon compounds are satisfactorily offset.

The average deviation in Figure 4 is 25%, and to place this value in perspective, we compare (in Table I) our vapor pressure data with values reported by Sonnefeld et al. (15). A procedural difference was that Sonnefeld et al. (15) coupled their trap directly to their hplc, a refinement that greatly improved precision. The degree of correspondence between the two sets of data (at 25°C) in Table I is similar to the uncertainty of the Figure 4 relationship. Thus, eq 5 offers a general and reliable route to vapor pressure, especially for relatively involatile compounds where the uncertainty of measurement is high. Other correlations of equal or greater accuracy have been reported (1-6,16), but only for closely related compounds of relatively high vapor pressure.

In summary, we have shown that solvatochromic parameters can be used to estimate vapor pressure. We have developed two addi-

tional relationships based on UNIFAC. One is intended for situations where the boiling point is unavailable, but it does not apply to silicon containing compounds. The other includes boiling point and is much more general with an average error of 25%.

Acknowledgments

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Literature Cited

1. Mackay, D.; Bobra, A.; Chan D.W.; Shiu, W.Y. Environ. Sci. Technol. 1982, 16, 645-649.
2. Macknick, A.B.; Prausnitz, J.M. Ind. Eng. Chem. Fundam. 1979, 18, 348-351.
3. Edwards, D.R.; Prausnitz, J.M. Ind. Eng. Chem. Fundam. 1981, 20, 280-283.
4. Kelly, C.M.; Mathias, P.M.; Schweighardt, F.K. Ind. Eng. Chem. Res. 1988, 27, 1732-1736.
5. Jensen, T.; Fredenslund, A.; Rasmussen, P. Ind. Eng. Chem. Fundam. 1981, 20, 239-246.
6. Ben Yair, O.; Fredenslund, A. Ind. Eng. Chem. Process Des. Dec. 1983, 22, 433-436.
7. Banerjee, S.; Kamlet, M.J. unpublished results.
8. Kamlet, M.J.; Doherty, R.M.; Carr, P.W.; Mackay, D.; Abraham, M.H.; Taft, R.W. Environ. Sci. Technol. 1988, 22, 503-509.
9. Yalkowsky, S.H.; Valvani, S. J. Pharm. Sci., 1980, 69, 912-922.

10. Reid, R.C.; Prausnitz, J.M.; Poling, B.E. "The Properties of Gases & Liquids". Fourth Ed., McGraw-Hill, 1987.
11. Federal Register 1980 45, 77345.
12. Weininger, J. Chem. Inf. Comput. Sci. 1988, 28, 31-36.
13. Tiegs, D.; Gmehling, J.; Rasmussen P.; Fredenslund, A. Ind. Eng. Chem. Res. 1987, 27, 159-161.
14. Howard, P.H.; Hueber, A.E.; Mulesky, B.C.; Crisman, J.S.; Meylan, W.; Crosbie, E.; Gray, D.A.; Sage, G.W.; Howard, K.P.; LaMacchia, A.; Boethling, R.; Troast, R. Environ. Toxicol. Chem. 1986, 5, 977-988.
15. Sonnefeld, W.J.; Zoller, W.H.; May, W.E. Anal. Chem. 1983, 55, 275-280.
16. Hansen, P.J.; Jurs, P.C. Anal. Chem. 1987, 59, 2322-2327.

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Captions to Figures

Figure 1. Correlation of Vapor Pressure with eq 1. Compounds included are acenaphthene, acetophenone, anthracene, benzaldehyde, benz(a)anthracene, benzene, benzonitrile, biphenyl, butanol, 2-butanol, 2-butanone, carbon tetrachloride, chlorobenzene, chloroform, p-cymene, DDT, decachlorobiphenyl, m-dichlorobenzene, 2,4'-dichlorobiphenyl, 1,2-dichloroethane, diethyl ether, dimethylacetamide, di-n-butyl ether, dimethyl formamide, dimethyl sulfoxide, ethyl acetate, ethylbenzene, fluorene, heptanol, hexachlorobenzene, 2,2',4,4',5,5'-hexachlorobiphenyl, hexanol, methyl acetate, methylene chloride, naphthalene, nitrobenzene, nitromethane, 2,2',3,3',5,5',6,6'-octachlorobiphenyl, octanol, pentachlorobenzene, phenanthrene, propylbenzene, pyrene, pyridine, 1,2,3,5-tetrachlorobenzene, 2,2',5,5'-tetrachlorobiphenyl, 1,1,2,2-tetrachloroethane, tetrahydrofuran, toluene, 1,3,5-trichlorobenzene, 1,1,1-trichloroethane, triethylamine, p-xylene.

Figure 2. Correlation of Vapor Pressure with eq 3.

Figure 3. Correlation of Boiling Point with eq 4.

Figure 4. Correlation of Vapor Pressure with eq 5.

Table I. Vapor Pressures of Some Compounds

	vapor pressure (mm) ± (%sd)		
	25°C[a]	25°C	35°C
aniline	6.0E-1 (8)	5.5E-1 (10)	1.53 (2)
anthracene		2.7E-6 (18)	7.4E-6 (5)
benzaldehyde		3.2 (16)	3.6 (10)
benzoic acid	8.17E-4 (5)	4.9E-4 (14)	3.8E-3 (8)
DDT		2.2E-6 (37)[b]	1.8E-5 (130)[b]
dibutyl phthalate		1.1E-4 (87)[b]	1.3E-4 (67)[b]
2,4-dinitrotoluene		7.3E-4 (54)	7.6E-3 (24)
2-nitrophenol	9.29E-2 (2)	1.1E-1 (39)[b]	4.7E-1 (16)
naphthalene	7.79E-2 (2)	1.2E-1 (24)	2.5E-1 (14)
phenanthrene	1.21E-4 (2)	1.1E-4 (39)	1.7E-4 (4)

[a]from ref. (15)
[b]possible underestimates

Table II. Estimation of vapor pressure with eq 3 and eq 5.

	mp	bp	VP_{meas} [a]	$VP_{eq\ 3}$ [a]	$VP_{eq\ 5}$ [a]
decachlorobiphenyl	305		3.97E-10	1.65E-10	
benzopyrene	176	495	5.49E-09	5.26E-09	1.23E-08
methyl cholanthrene	179		7.73E-09	3.36E-09	
benzanthracene	160	438	3.05E-08	2.54E-07	2.35E-07
22'33'55'66'-octachlorobiphenyl	162		2.17E-07	4.47E-08	
beta-hexachlorocyclohexane	314		4.66E-07	1.17E-05	
pyrene	150	404	2.50E-06	1.30E-06	1.81E-06
anthracene	216	340	2.70E-06	9.39E-06	7.01E-06
butyl benzyl phthalate		370	8.25E-06	8.50E-06	1.80E-05
22'455'-pentachlorobiphenyl	77		8.32E-06	1.14E-05	
hexachlorobenzene	229	332	1.80E-05	4.03E-05	4.72E-06
delta-hexachlorocyclohexane	142		3.52E-05	6.13E-04	
dibutylphthalate		340	7.30E-05	1.83E-04	8.51E-05
3-nitroaniline	114		9.56E-05	1.65E-02	
2'34-trichlorobiphenyl	60		1.03E-04	2.04E-04	
phenanthrene	100	340	1.12E-04	1.36E-04	1.01E-04
ß-naphthylamine	112	306	2.60E-04	2.55E-03	3.38E-04

Table II (contd.)	mp	bp	VP_{meas} [a]	$VP_{eq\ 3}$ [a]	$VP_{eq\ 5}$ [a]
26-dinitrotoluene	71		5.67E-04	7.56E-03	
diethylphthalate		299	1.65E-03	2.94E-03	1.09E-03
dimethyl phthalate		282	1.65E-03	1.01E-02	3.13E-03
acenaphthene	94	279	2.30E-03	9.15E-04	2.15E-03
26-diaminotoluene	105	260	2.46E-03	1.17E-02	2.31E-03
toluenediamine	105	255	2.46E-03	1.17E-02	2.88E-03
1245~tetrachlorobenzene	140	243	5.40E-03	4.61E-03	2.82E-03
biphenyl	87	255	8.90E-03	4.79E-03	6.26E-03
dimethyl terephthalate	141		1.00E-02	8.66E-04	
4-chloroaniline	69	232	2.50E-02	0.24E+00	2.83E-02
naphthalene	80	218	8.50E-02	3.52E-02	5.15E-02
ethylene glycol		197	9.20E-02	5.90E-04	4.26E-02
quinoline		237	9.60E-02	4.61E-02	8.26E-02
decylamine		217	0.10E+00	0.10E+00	7.07E-02
p-cresol		202	0.11E+00	0.88E+00	0.30E+00
cyclohexanol		160	0.11E+00	1.47E+00	1.50E+00
26-dimethylaniline		214	0.13E+00	0.27E+00	0.15E+00
2-ethyl-1-hexanol		185	0.14E+00	0.22E+00	0.31E+00
nitrobenzene		210	0.25E+00	1.80E+00	0.23E+00

Table II (contd.)	mp	bp	VP_{meas} [a]	$VP_{eq\ 3}$ [a]	$VP_{eq\ 5}$ [a]
o-chloroaniline		209	0.26E+00	0.65E+00	0.22E+00
o-toluidine		200	0.32E+00	0.85E+00	0.33E+00
phenol	41	182	0.35E+00	2.15E+00	0.58E+00
acetophenone		202	0.37E+00	0.57E+00	0.27E+00
isophorone		213	0.40E+00	0.64E+00	0.13E+00
aniline		184	0.49E+00	2.85E+00	0.77E+00
NN-dimethylaniline		193	0.52E+00	0.42E+00	0.42E+00
trichloroacetic acid	51	126	1.00E+00	3.68E+00	4.77E+00
benzyl chloride		179	1.30E+00	1.53E+00	0.98E+00
anisole		154	1.53E+00	2.87E+00	2.97E+00
bis-2-chloroethylether			1.55E+00	6.43E+00	
123-trichlorobenzene	54	218	2.10E+00	0.14E+00	7.52E-02
trimethylbenzene		168	2.10E+00	0.53E+00	1.36E+00
m-dichlorobenzene		172	2.15E+00	1.20E+00	1.36E+00
indene		182	2.23E+00	0.36E+00	0.96E+00
123-trichloropropane		156	3.10E+00	7.20E+00	2.54E+00
propionic acid		141	3.40E+00	6.57E+01	5.95E+00
chlorotoluene		158	3.43E+00	1.48E+00	2.55E+00

Table II (contd.)	mp	bp	VP_{meas} [a]	$VP_{eq\ 3}$ [a]	$VP_{eq\ 5}$ [a]
pentachloroethane		161	3.50E+00	3.40E+00	1.88E+00
dimethyl formamide		153	3.70E+00	1.33E+01	2.66E+00
acrylic acid		139	4.00E+00	9.40E+01	6.70E+00
cyclohexanone		155	4.50E+00	6.28E+00	2.83E+00
cumene		153	4.50E+00	0.75E+00	2.70E+00
alpha-pinene		155	5.00E+00	0.38E+00	2.00E+00
bromoform		150	5.40E+00	8.41E+00	3.17E+00
2-ethoxyethanol		135	5.63E+00	3.31E+00	4.75E+00
1122-tetrachloroethane		147	6.10E+00	7.92E+00	4.07E+00
styrene		146	6.40E+00	2.51E+00	4.59E+00
xylene		138	6.62E+00	1.73E+00	6.15E+00
butanol		118	6.70E+00	7.49E+00	1.19E+01
2-methoxyethanol		124	9.50E+00	6.32E+00	8.49E+00
ethylbenzene		136	9.60E+00	2.12E+00	6.80E+00
morpholine		129	1.00E+01	1.97E+01	1.05E+01
acetic acid		117	1.14E+01	2.45E+02	1.92E+01
2-hexanone		127	1.16E+01	4.58E+00	8.03E+00
chlorobenzene		132	1.20E+01	5.74E+00	9.66E+00
2-methyl-2-butanol		102	1.20E+01	3.04E+00	2.05E+01

Table II (contd.)	mp	bp	VP_{meas} [a]	$VP_{eq\ 3}$ [a]	$VP_{eq\ 5}$ [a]
chloroacetone		120	1.20E+01	2.26E+01	1.31E+01
1-methoxy-2-propanol		118	1.25E+01	2.61E+00	9.63E+00
isobutanol		108	1.26E+01	7.56E+00	1.84E+01
12-dibromoethane		131	1.42E+01	2.85E+01	8.99E+00
butyl acetate		125	1.50E+01	4.76E+00	8.72E+00
2-nitropropane		120	1.80E+01	3.05E+01	1.43E+01
2-butanol		99	1.83E+01	7.48E+00	2.69E+01
tetrachloroethylene		121	1.86E+01	3.24E+01	1.43E+01
methyl isobutyl ketone		117	1.99E+01	4.54E+00	1.25E+01
pyridine		115	2.08E+01	1.24E+01	2.41E+01
112-trichloroethane		147	2.30E+01	2.79E+01	4.66E+00
water		100	2.38E+01	6.87E+01	3.50E+01
ethyl acetate		77	2.43E+01	3.93E+01	1.01E+02
allyl alcohol		97	2.81E+01	2.88E+01	3.62E+01
toluene		111	2.84E+01	6.41E+00	2.43E+01
13-dichloropropene		106	3.40E+01	5.77E+01	3.20E+01
crotonaldehyde		104	3.80E+01	5.43E+01	3.09E+01
dioxane		101	3.81E+01	4.57E+01	3.85E+01

Table II (contd.)	mp	bp	VP_{meas}[a]	$VP_{eq\ 3}$[a]	$VP_{eq\ 5}$[a]
t-butanol		83	4.20E+01	7.56E+00	5.60E+01
formic acid		100	4.26E+01	5.09E+02	3.71E+01
trichloroacetaldehyde		98	5.00E+01	3.14E+00	2.56E+01
12-dichloropropane		96	5.33E+01	3.35E+01	4.66E+01
ethanol		78	5.93E+01	6.01E+01	9.27E+01
12-dichloroethane		83	8.20E+01	1.04E+02	9.09E+01
acetonitrile		82	8.88E+01	3.12E+02	8.57E+01
benzene		80	9.52E+01	2.81E+01	1.14E+02
methyl ethyl ketone		80	9.53E+01	4.07E+01	8.74E+01
cyclohexane		81	9.69E+01	1.30E+01	8.87E+01
acrylonitrile		77	1.09E+02	1.17E+02	1.03E+02
carbon tetrachloride		77	1.15E+02	6.87E+01	1.18E+02
111-trichloroethane		75	1.24E+02	7.20E+00	9.29E+01
methanol		65	1.27E+02	1.27E+03	2.03E+02
methylcyclopentane		72	1.38E+02	1.28E+01	1.33E+02
diisopropyl ether		68	1.49E+02	8.14E+00	1.24E+02
hexane		69	1.52E+02	1.17E+01	1.28E+02
11-dimethoxyethane		64	1.71E+02	2.12E+01	1.61E+02
isobutyraldehyde		63	1.73E+02	4.75E+01	1.92E+02

Table II (contd.)	mp	bp	VP_{meas}[a]	$VP_{eq\ 3}$[a]	$VP_{eq\ 5}$[a]
chloroform		61	1.97E+02	1.37E+02	2.62E+02
cis-12-dichloroethylene		60	2.01E+02	2.52E+02	2.90E+02
aziridine		56	2.13E+02	9.69E+02	3.99E+02
acetone		56	2.32E+02	1.45E+02	2.88E+02
acrolein		53	2.73E+02	1.76E+02	3.24E+02
propionaldehyde		48	3.17E+02	1.74E+02	4.26E+02
3-chloropropene		45	3.68E+02	2.23E+02	5.56E+02
2-methyl-13-butadiene		34	5.50E+02	8.08E+01	7.77E+02
acetaldehyde		21	9.02E+02	7.74E+02	1.56E+03
trimethylamine			1.43E+03	1.64E+02	

[a] in mm

Table III. Some outliers from equations 3,4 and 5

	Δlog VP[a] (eq 3)	Δlog VP[a] (eq 5)	ΔBP[ab] (eq 4)
acetic acid	1.33	0.22	- 58
diisopropyl ether	-1.26	-0.09	62
ethylene glycol	-2.19	-0.33	77
formic acid	1.08	-0.06	- 61
hexamethyldisiloxane[c]	3.04	-0.07	-156
hexane	-1.11	-0.09	55
octamethyltetrasiloxane[c]	4.68	0.65	-203
propionic acid	1.29	0.25	- 56
1,1,1-trichloroethane	-1.24	-0.14	57

[a]measured minus estimated values; [b]in ^{o}C;
[c]excluded from the regressions for equations 3 and 4.

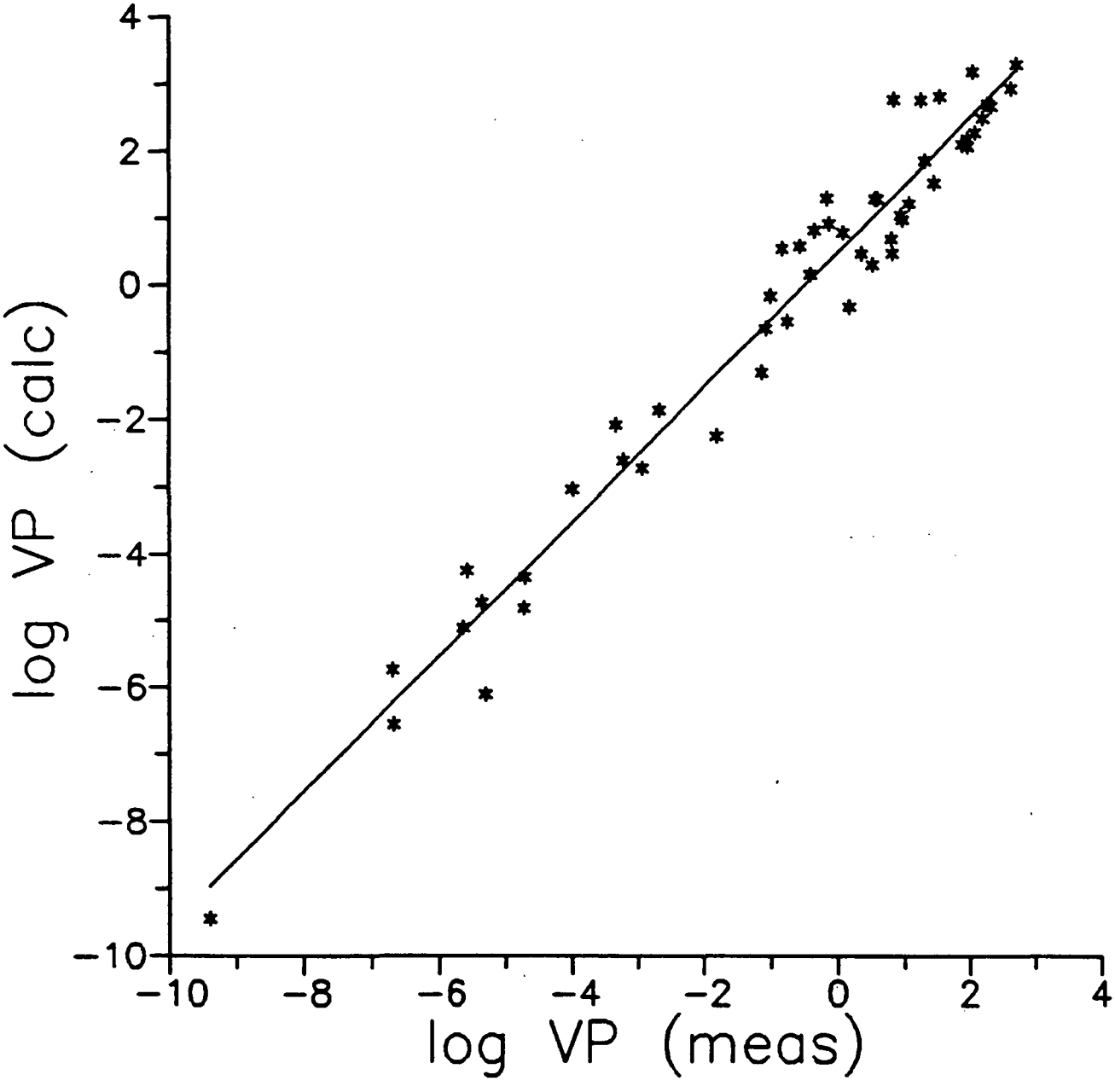

Figure 1.

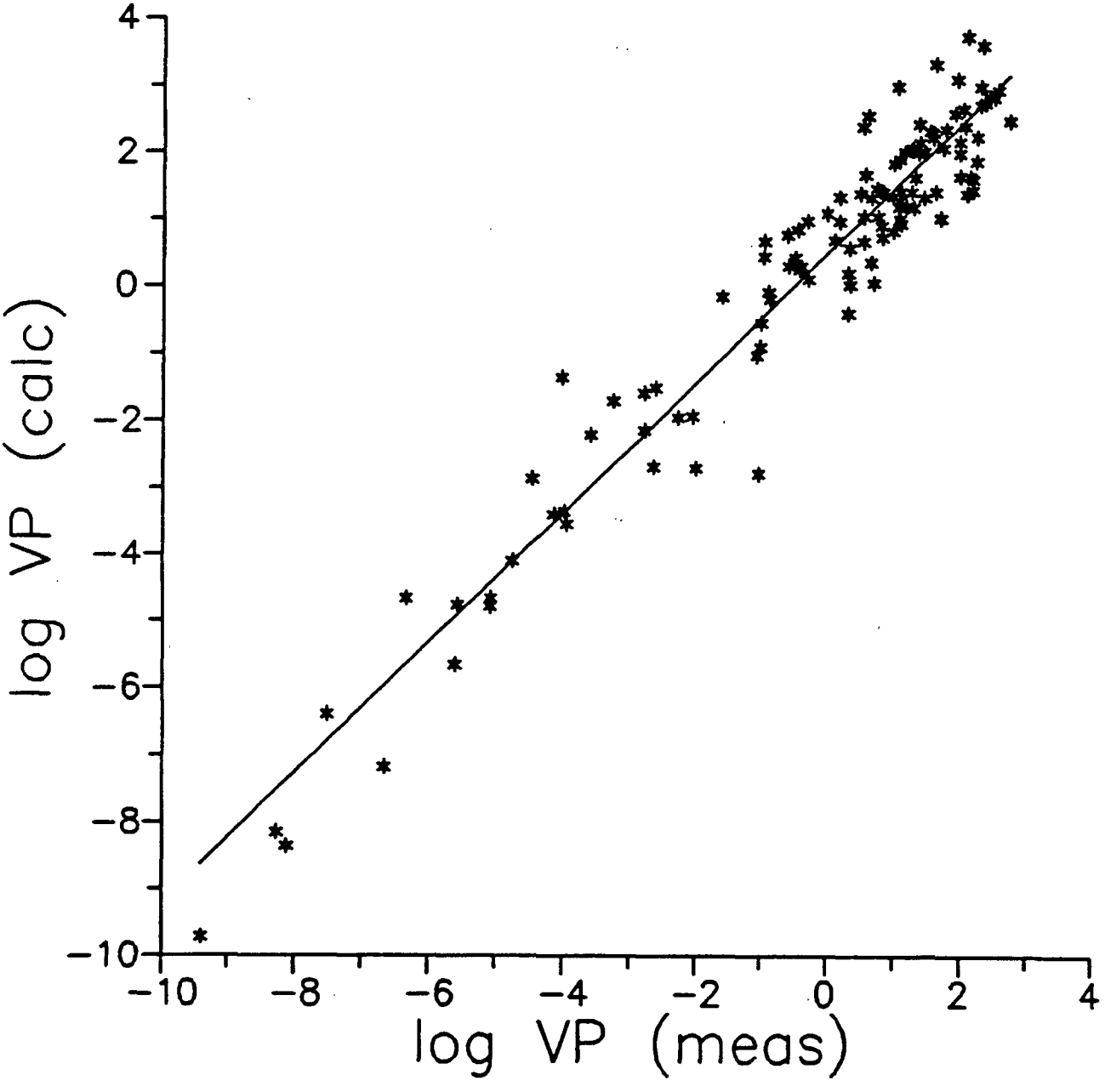

Figure 2.

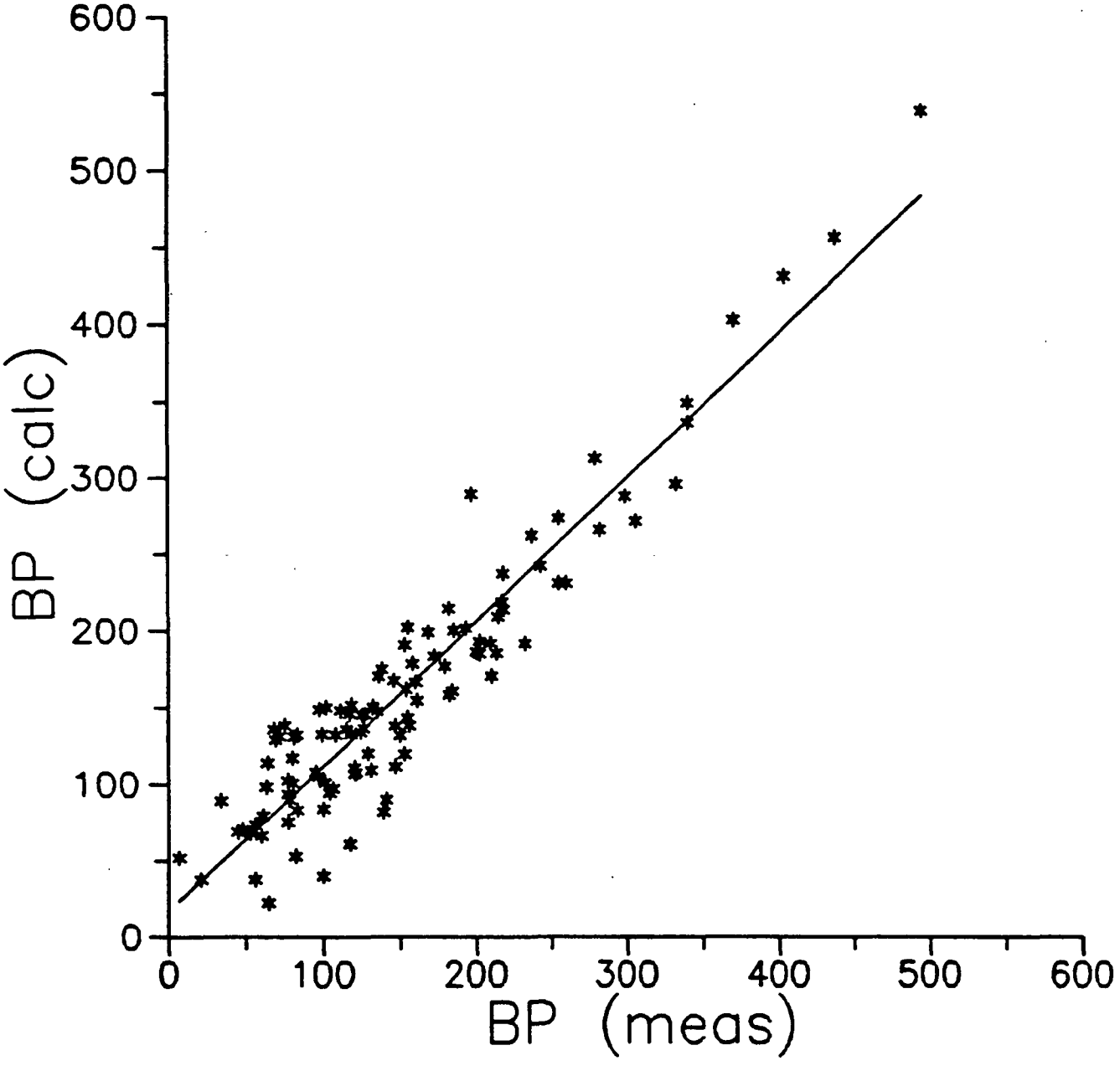
600
500
400
300
200
100
0
BP (calc)
0
100
200
300
400
500
600
BP (meas)

Figure 3.

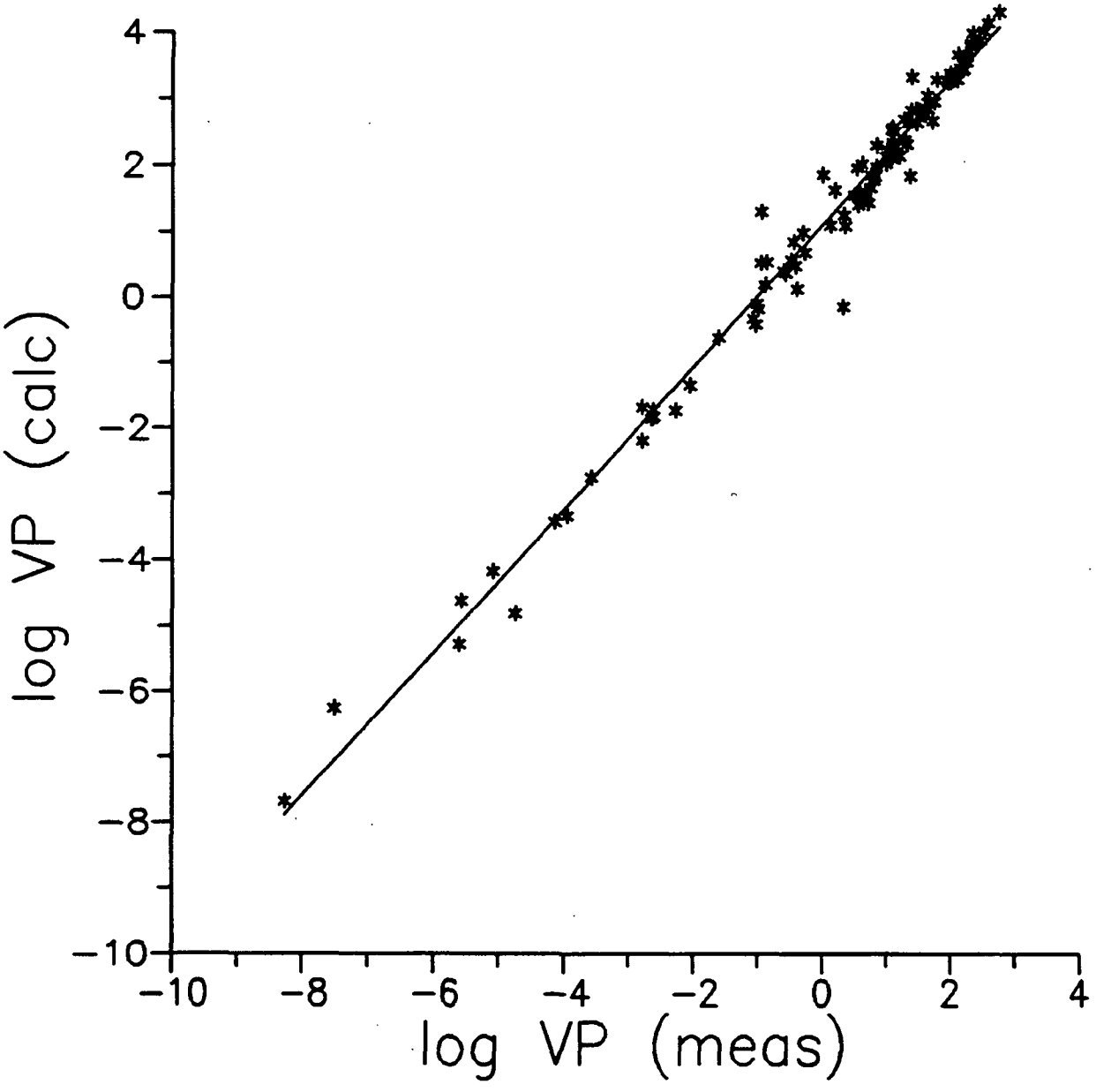

Figure 4.